



# DECLARATION

I, Osamu MAEDA, c/o the Inoue & Associates of 3rd Floor, Akasaka Habitation Building, 3-5, Akasaka 1-chome, Minato-ku, Tokyo, Japan do solemnly and sincerely declare that I am conversant with the Japanese and English languages and that I have executed with the best of my ability this translation into English of the Certified Copy of Japanese Patent Application No. 2002-122931 and believe that the translation is true and correct.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

March 10, 2008

(Date)

Osamu Maeda

Osamu MAEDA

JAPAN PATENT OFFICE

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[Inventor]

[Address] c/o Asahi Kasei Kabushiki Kaisha,  
3-1, Yakou 1-chome, Kawasaki-ku,  
Kawasaki-shi, Kanagawa-ken

[Name] Shigeo NAKAJIMA

[Inventor]

[Address] c/o Asahi Kasei Kabushiki Kaisha,  
3-1, Yakou 1-chome, Kawasaki-ku,  
Kawasaki-shi, Kanagawa-ken

[Name] Toshinori Shiraki

[Applicant for Patent]

[Identification Number] 000000033

[Name] Asahi Kasei Kabushiki Kaisha

[Representative] Kazumoto Yamamoto

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[Name of Document] Specification

[Title of the Invention] Asphalt composition

[Scope of Claims for Patent]

[Claim 1] An asphalt composition comprising:

0.5 to 50 parts by weight of a modified block copolymer or hydrogenation product thereof as component (1-1), said modified block copolymer comprising:

at least one polymer block A composed mainly of vinyl aromatic hydrocarbon monomer units,

at least one polymer block B composed mainly of conjugated diene monomer units, and

at least one modifier group having at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, an amino group, a silanol group and an alkoxysilane group,

said modifier group being bonded to at least one member selected from the group consisting of said polymer block A and said polymer block B,

100 parts by weight of an asphalt as component (2), and 0.01 to 10 parts by weight of sulfur as component (3).

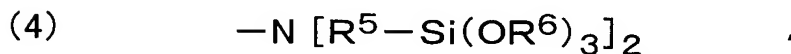
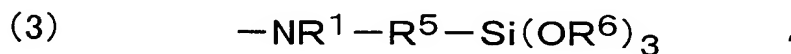
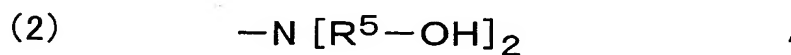
[Claim 2] An asphalt composition comprising:

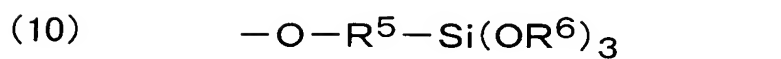
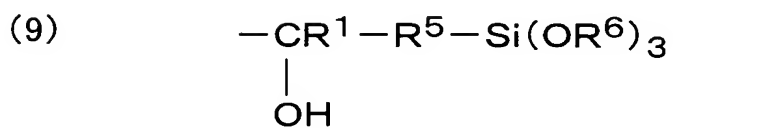
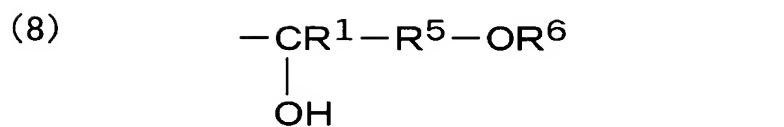
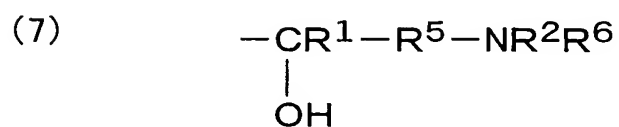
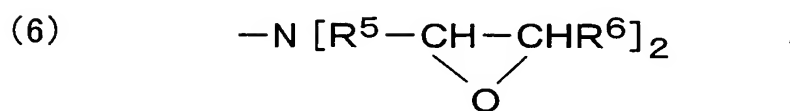
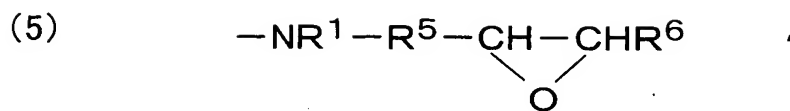
0.5 to 50 parts by weight of a second-order modified block copolymer as component (1-2), said second-order modi-

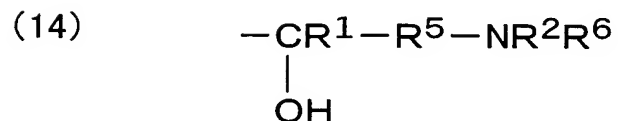
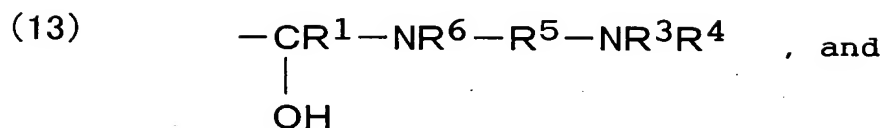
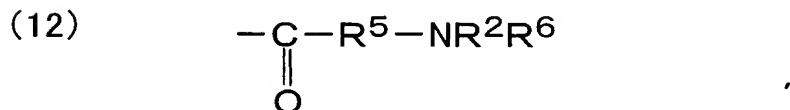
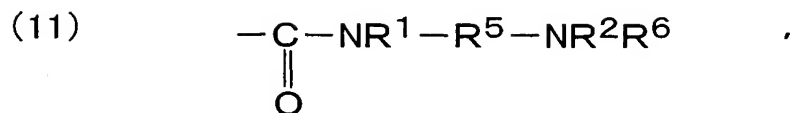
fied block copolymer being obtained by reacting a component (1-1) with a crosslinking agent (4) in an amount of 0.3 to 10 mol, relative to one equivalent of the functional group of said component (1-1),

100 parts by weight of an asphalt as component (2), and 0.01 to 10 parts by weight of sulfur as component (3).

[Claim 3] The asphalt composition according to claim 1 or 2, wherein said modifier group has at least one functional group selected from the group consisting of the functional groups represented by the following formulae (1) to (14):







wherein, in the formulae (1) to (14):

each of  $\text{R}^1$  to  $\text{R}^4$  independently represents a hydrogen atom or a  $\text{C}_1$ - $\text{C}_{24}$  hydrocarbon group which optionally has at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, a silanol group and an alkoxysilane group,



each  $R^5$  independently represents a  $C_1$ - $C_{48}$  hydrocarbon group which optionally has at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, a silanol group and an alkoxysilane group, and each  $R^6$  independently represents a hydrogen atom or a  $C_1$ - $C_8$  alkyl group,

wherein said hydrocarbon group as each of  $R^1$  to  $R^5$  optionally has bonded thereto at least one atom selected from the group consisting of an oxygen atom, a nitrogen atom and a silicon atom, said at least one atom being present in a form which is different from those of a hydroxyl group, an epoxy group, a silanol group and an alkoxysilane group.

[Claim 4] The asphalt composition according to claim 2 or 3, wherein said crosslinking agent (4) is a crosslinking agent having at least one functional group selected from the group consisting of a carboxyl group, an acid anhydride group, an isocyanate group, an epoxy group, a silanol group and an alkoxysilane group.

[Claim 5] The asphalt composition according to any one of claims 1 to 4, wherein said modified block copolymer is

produced by bonding a modifier having a functional group to a living lithium terminal of a block copolymer which is obtained by a polymerization reaction performed in the presence of an organolithium compound as a polymerization catalyst.

[Claim 6] The asphalt composition according to any one of claims 1 to 4, wherein the hydrogenation product of said modified block copolymer is produced by bonding a modifier having a functional group to a living lithium terminal of a block copolymer, followed by hydrogenation, wherein said block copolymer is obtained by a polymerization reaction performed in the presence of an organolithium compound as a polymerization catalyst.

[Detailed Description of the Invention]

[0001]

[Application Field in Industry]

The present invention relates to an asphalt composition having a high softening point and excellent properties with respect to ductility, flexural properties, aggregate-gripping properties, and storage stability at high temperatures. More particularly, the present invention is concerned with an asphalt composition comprising a block copolymer or hydrogenation product thereof, an asphalt and sulfur, wherein the block copolymer comprises vinyl aromatic hydrocarbon monomer

units, conjugated diene monomer units and a specific functional group.

[0002]

[Prior Art]

Conventionally, an asphalt composition has been used in a wide variety of fields, such as the fields of a material for use in road paving, a material for a waterproof sheet, a material for a sound insulating sheet and a roofing material. In these fields, a number of attempts have been made to improve the properties of the asphalt composition by adding various polymers to the asphalt composition. As examples of such polymers, there can be mentioned an ethylene/vinyl acetate copolymer, an ethylene/ethyl acrylate copolymer, a rubber latex, and a block copolymer comprising conjugated diene monomer units and vinyl aromatic hydrocarbon monomer units.

[0003]

However, in recent years, due to the expansion of traffic and the increase in the number of expressways, there is a growing demand for an asphalt mixture having excellent strength and excellent abrasion resistance. Further, there is a growing demand for an asphalt mixture which not only has excellent strength and excellent abrasion resistance, but also can be used to form a highly open graded pavement layer

which can improve the drainage properties and noise reduction properties of expressways. For achieving the above-mentioned excellent properties, the asphalt composition is required to have a high softening point and high mechanical strengths (such as high flexural stress and excellent aggregate-gripping properties). For meeting this requirement, it has been attempted, for example, to employ a method in which a block copolymer having a high molecular weight is incorporated into the asphalt composition. However, such method is disadvantageous in that the resultant asphalt composition containing a high molecular weight block copolymer incorporated therein has unsatisfactory storage stability at high temperatures and, hence, its melt viscosity becomes increased under high temperature conditions, thus rendering poor the workability of the asphalt composition during the road paving.

[0004]

For improving the storage stability of an asphalt composition at high temperatures, it has generally been attempted to add an aromatic process oil to the asphalt composition, or effect a crosslinking of the asphalt composition by the use of sulfur or a peroxide. For example, Examined Japanese Patent Application Publication No. Sho 57-24385 discloses a crosslinking using sulfur. On the other hand, Examined Japa-

nese Patent Application Publication No. Hei 1-13743 discloses a crosslinking using a polysulfide having a specific structure. Further, Unexamined Japanese Patent Application Laid-Open Specification No. Hei 3-501035 discloses a crosslinking using a combination of sulfur, a vulcanizing agent, and a sulfur-containing compound as a vulcanization accelerator.

[0005]

[Problems to Be Solved by the Invention]

However, any of the above-mentioned techniques is still unsatisfactory in improving the storage stability of an asphalt composition at high temperatures. Thus, it has been desired to develop an asphalt composition which has not only a high softening point, excellent flexural properties and excellent aggregate-gripping properties, but also excellent storage stability at high temperatures.

[0006]

[Means to Solve the Problems]

The present inventors have made extensive and intensive studies with a view toward solving the above-mentioned problems accompanying the prior art. In their studies, the present inventors have focused on improvement of the properties of an asphalt composition containing a block copolymer or hy-

hydrogenation product thereof comprising vinyl aromatic hydrocarbon monomer units and conjugated diene monomer units, and an asphalt. As a result, it has unexpectedly been found that, when the asphalt composition block comprises an asphalt, a modified block copolymer or hydrogenation product thereof (wherein the modified block copolymer has a specific functional group), and sulfur, the asphalt composition has a high softening point and excellent properties with respect to ductility, flexural properties, aggregate-gripping properties, and storage stability at high temperatures. Based on this finding, the present invention has been completed.

[0007]

That is, the present invention is as follows:

1. An asphalt composition comprising:

0.5 to 50 parts by weight of a modified block copolymer or hydrogenation product thereof as component (1-1), the modified block copolymer comprising:

at least one polymer block A composed mainly of vinyl aromatic hydrocarbon monomer units,

at least one polymer block B composed mainly of conjugated diene monomer units, and

at least one modifier group having at least one functional group selected from the group consisting of a hydroxyl

group, an epoxy group, an amino group, a silanol group and an alkoxysilane group,

the modifier group being bonded to at least one member selected from the group consisting of the polymer block A and the polymer block B,

100 parts by weight of an asphalt as component (2), and  
0.01 to 10 parts by weight of sulfur as component (3).

[0008]

2. An asphalt composition comprising:

0.5 to 50 parts by weight of a second-order modified block copolymer as component (1-2), the second-order modified block copolymer being obtained by reacting a component (1-1) with a crosslinking agent (4) in an amount of 0.3 to 10 mol, relative to one equivalent of the functional group of the component (1-1),

100 parts by weight of an asphalt as component (2), and  
0.01 to 10 parts by weight of sulfur as component (3).

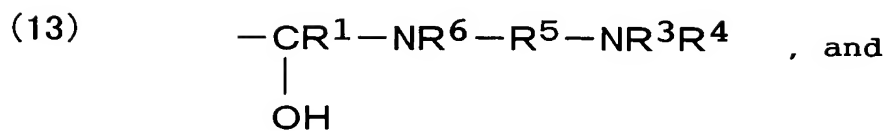
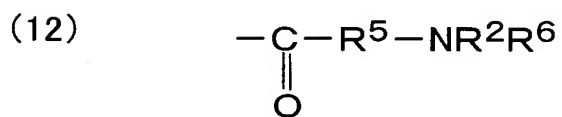
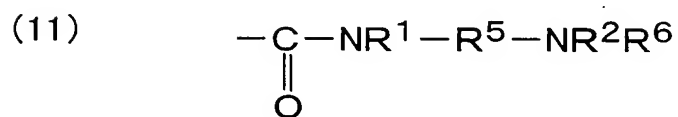
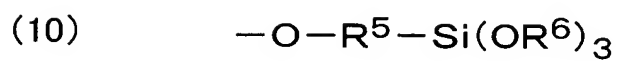
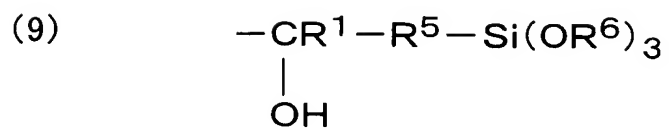
[0009]

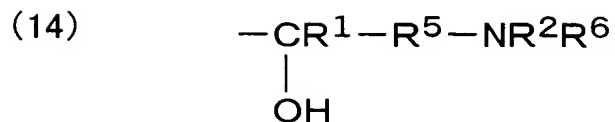
3. The asphalt composition according to item 1 or 2 above, wherein the modifier group has at least one functional group selected from the group consisting of the functional groups represented by the following formulae (1) to (14):

[0010]

- (1)  $-\text{NR}^1-\text{R}^5-\text{OH}$
- (2)  $-\text{N} [\text{R}^5-\text{OH}]_2$
- (3)  $-\text{NR}^1-\text{R}^5-\text{Si}(\text{OR}^6)_3$
- (4)  $-\text{N} [\text{R}^5-\text{Si}(\text{OR}^6)_3]_2$
- (5)  $-\text{NR}^1-\text{R}^5-\text{CH}-\text{CHR}^6$   
                                 $\diagdown \quad \diagup$   
                                O
- (6)  $-\text{N} [\text{R}^5-\text{CH}-\text{CHR}^6]_2$   
                                 $\diagdown \quad \diagup$   
                                O
- (7)  $-\text{CR}^1-\text{R}^5-\text{NR}^2\text{R}^6$   
      |  
      OH
- (8)  $-\text{CR}^1-\text{R}^5-\text{OR}^6$   
      |  
      OH







[0011]

wherein, in the formulae (1) to (14):

each of  $\text{R}^1$  to  $\text{R}^4$  independently represents a hydrogen atom or a  $\text{C}_1$ - $\text{C}_{24}$  hydrocarbon group which optionally has at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, a silanol group and an alkoxysilane group,

each  $\text{R}^5$  independently represents a  $\text{C}_1$ - $\text{C}_{48}$  hydrocarbon group which optionally has at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, a silanol group and an alkoxysilane group, and

each  $\text{R}^6$  independently represents a hydrogen atom or a  $\text{C}_1$ - $\text{C}_8$  alkyl group,

wherein the hydrocarbon group as each of  $\text{R}^1$  to  $\text{R}^5$  optionally has bonded thereto at least one atom selected from the group consisting of an oxygen atom, a nitrogen atom and a silicon atom,

the at least one atom being present in a form which is different from those of a hydroxyl group, an epoxy group, a silanol group and an alkoxysilane group.

[0012]

4. The asphalt composition according to item 2 or 3 above, wherein the crosslinking agent (4) is a crosslinking agent having at least one functional group selected from the group consisting of a carboxyl group, an acid anhydride group, an isocyanate group, an epoxy group, a silanol group and an alkoxysilane group.

[0013]

5. The asphalt composition according to any one of items 1 to 4 above, wherein the modified block copolymer is produced by bonding a modifier having a functional group to a living lithium terminal of a block copolymer which is obtained by a polymerization reaction performed in the presence of an organolithium compound as a polymerization catalyst.

[0014]

6. The asphalt composition according to any one of items 1 to 4 above, wherein the hydrogenation product of the modified block copolymer is produced by bonding a modifier having a functional group to a living lithium terminal of a block

copolymer, followed by hydrogenation, wherein the block copolymer is obtained by a polymerization reaction performed in the presence of an organolithium compound as a polymerization catalyst.

[0015]

Hereinbelow, the present invention is explained in detail.

With respect to the block copolymer or hydrogenation product thereof comprising vinyl aromatic hydrocarbon monomer units and conjugated diene monomer units, used in the present invention, the amount of vinyl aromatic hydrocarbon monomer units in the block copolymer or hydrogenation product thereof is generally from 5 to 95 % by weight, preferably from 10 to 90 % by weight, more preferably from 15 to 85 % by weight. It is especially recommended that the amount of vinyl aromatic hydrocarbon monomer units in the block copolymer or hydrogenation product thereof is from 5 to 60 % by weight, preferably from 10 to 55 % by weight, more preferably from 15 to 50 % by weight.

[0016]

As examples of methods for producing the block copolymer, there can be mentioned the methods described in Examined Japanese Patent Application Publication Nos. Sho 36-19286,

Sho 43-17979, Sho 46-32415, Sho 49-36957, Sho 48-2423, Sho 48-4106 and Sho 51-49567 and Unexamined Japanese Patent Application Laid-Open Specification No. Sho 59-166518. By any of the methods described in the above-mentioned patent documents, the block copolymer can be produced in the form of a living block copolymer. By a reaction of a living terminal of the block copolymer with the below-described modifier compound, the modified block copolymer having a functional group, used in the present invention, can be obtained. The modified block copolymer used in the present invention has, for example, a structure represented by a formula selected from the group consisting of the following formulae:

[0017]

$(A-B)_n-Y$ ,  $A-(B-A)_n-Y$ ,  $B-(A-B)_n-Y$ ,  $Y-(A-B)_n$ ,  $Y-(A-B)_n-Y$ ,  
 $Y-A-(B-A)_n-Y$ ,  $Y-B-(A-B)_n-Y$ ,  $[(B-A)_n]_{m+1}-Y$ ,  $[(A-B)_n]_{m+1}-Y$ ,  
 $[(B-A)_n-B]_{m+1}-Y$ , and  $[(A-B)_n-A]_{m+1}-Y$ .

(In the above-mentioned formulae, each A independently represents a polymer block composed mainly of vinyl aromatic hydrocarbon monomer units, and each B independently represents a polymer block composed mainly of conjugated diene monomer units. It is not necessary that the boundary between the polymer blocks A and B be distinct. In the above-mentioned formulae, n is a positive number of 1 or more, generally an

integer of from 1 to 5, and m is a positive number of 1 or more, generally an integer of from 1 to 10. Each Y independently represents a residue (i.e., modifier group) of the below-described modifier compound which has at least one functional group. When Y is bonded to the polymer block A and/or the polymer block B by the below-described method including a metalation reaction, Y is bonded to a side chain of the polymer block A and/or the polymer block B. The structures of the polymer chains each having Y bonded thereto are the same or different.)

[0018]

In the present invention, a polymer block A composed mainly of vinyl aromatic hydrocarbon monomer units is a copolymer block comprising vinyl aromatic hydrocarbon monomer units and conjugated diene monomer units or a homopolymer block comprising vinyl aromatic hydrocarbon monomer units, wherein the amount of vinyl aromatic hydrocarbon monomer units in the copolymer block is 50 % by weight or more, preferably 70 % by weight or more. A polymer block B composed mainly of conjugated diene monomer units is a copolymer block comprising conjugated diene monomer units and vinyl aromatic hydrocarbon monomer units or a homopolymer block comprising conjugated diene monomer units, wherein the amount of conju-

gated diene monomer units in the copolymer block is more than 50 % by weight, preferably 70 % by weight or more.

[0019]

The vinyl aromatic hydrocarbon monomer units may be uniformly distributed or may be distributed in a tapered configuration in the copolymer block. The copolymer block may have a plurality of segments in which the vinyl aromatic hydrocarbon monomer units are uniformly distributed, and/or may have a plurality of segments in which the vinyl aromatic hydrocarbon monomer units are distributed in a tapered configuration. The block copolymer used in the present invention may be a mixture of a plurality of block copolymers having structures selected from the group consisting of the structures represented by the above-mentioned formulae.

[0020]

When the modified block copolymer or hydrogenation product thereof has at least one vinyl aromatic hydrocarbon homopolymer block, from the viewpoint of obtaining an asphalt composition having excellent ductility, it is preferred that the ratio of the weight of the at least one vinyl aromatic hydrocarbon homopolymer block to the total weight of the vinyl aromatic hydrocarbon monomer units in the modified block copolymer or hydrogenation product thereof (hereinafter re-

ferred to as "vinyl aromatic hydrocarbon block ratio") is controlled in the range of from 50 % by weight or more, more advantageously from 50 to 97 % by weight, still more advantageously from 60 to 95 % by weight.

[0021]

With respect to the weight average molecular weight of the at least one vinyl aromatic hydrocarbon homopolymer block, it is recommended that the weight average molecular weight is generally from 5,000 to 500,000, preferably from 7,000 to 200,000. The vinyl aromatic hydrocarbon block ratio can be measured by the following method. The weight of the at least one vinyl aromatic hydrocarbon homopolymer block is obtained by, for example, a method in which the unhydrogenated block copolymer is subjected to oxidative degradation using tert-butyl hydroperoxide in the presence of osmium tetroxide as a catalyst (i.e., the method described in I.M. KOLTHOFF, et al., J. Polym. Sci. 1, 429 (1946)). Using the obtained weight of the vinyl aromatic hydrocarbon homopolymer block, the vinyl aromatic hydrocarbon block ratio is calculated by the below-mentioned formula, with the proviso that, among the polymer chains (formed by the oxidative degradation) corresponding to the vinyl aromatic hydrocarbon homopolymer blocks, the polymer chains having a polymerization degree of about 30



or less are not taken into consideration in the measurement of the vinyl aromatic hydrocarbon block ratio.

Vinyl aromatic hydrocarbon block ratio (%)

= {(weight of the at least one vinyl aromatic hydrocarbon homopolymer block in the unhydrogenated block copolymer)/(total weight of the vinyl aromatic hydrocarbon monomer units in the unhydrogenated block copolymer)} × 100.

[0022]

In the present invention, the microstructure (including the amounts of a cis bond, a trans bond, and a vinyl bond) of the conjugated diene monomer units in the block copolymer can be appropriately controlled by using the below-described polar compound and the like. When 1,3-butadiene is used as the conjugated diene monomer, the 1,2-vinyl bond content is generally in the range of from 5 to 90 %. When isoprene is used as the conjugated diene monomer, the total content of the 1,2-vinyl bond and 3,4-vinyl bond is generally in the range of from 3 to 80 %. However, in the case where a hydrogenated block copolymer is used as the block copolymer, the microstructure of the conjugated diene monomer units in the block copolymer is controlled to be as follows. When 1,3-butadiene is used as the conjugated diene monomer, the 1,2-vinyl bond content is preferably in the range of from 10 to 80 %, more

preferably from 25 to 75 %. When isoprene is used as the conjugated diene monomer, the total content of the 1,2-vinyl bond and 3,4-vinyl bond is preferably in the range of from 5 to 70 %.

[0023]

In the present invention, the conjugated diene monomer is a diolefin having a pair of conjugated double bonds. Examples of conjugated diene monomers include 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and 1,3-hexadiene. Of these conjugated diene monomers, preferred are 1,3-butadiene and isoprene. These conjugated diene monomers can be used individually or in combination. Examples of vinyl aromatic hydrocarbon polymers include styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene,  $\alpha$ -methylstyrene, vinyl naphthalene and vinyl anthracene. Of these, styrene is preferred. These vinyl aromatic hydrocarbon monomers can be used individually or in combination.

[0024]

In the present invention, examples of solvents used in the production of the block copolymer include aliphatic hydrocarbons, such as butane, pentane, hexane, isopentane, heptane, octane and isooctane; alicyclic hydrocarbons, such as

cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane and ethylcyclohexane; and aromatic hydrocarbons, such as benzene, toluene, ethylbenzene and xylene. These solvents can be used individually or in combination.

[0025]

The organolithium compound used in the production of the block copolymer is an organic compound having at least one lithium atom in a molecule thereof. Examples of organolithium compounds include ethyllithium, n-propyllithium, isopropyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, hexamethylenedilithium, butadienyldilithium and isoprenenyldilithium. The above-mentioned organolithium compounds can be used individually or in combination. In the production of the block copolymer, all the amount of the organolithium compound may be added at one time, or the organolithium compound may be added portionwise at two or more times.

[0026]

In the present invention, for controlling the rate of the polymerization reaction for producing the block copolymer, for changing the microstructure of the conjugated diene segments in the base block copolymer produced, and for adjusting the reactivity ratio of the conjugated diene monomer to the

vinyl aromatic hydrocarbon monomer, a polar compound or a randomizing agent may be used. Examples of polar compounds and randomizing agents include ethers, amines, thioethers, phosphoramides, a potassium salt or sodium salt of an alkylbenzenesulfonic acid, and an alkoxide of potassium or sodium. Examples of ethers include dimethyl ether, diethyl ether, diphenyl ether, tetrahydrofuran, diethylene glycol dimethyl ether and diethylene glycol dibutyl ether. Examples of amines include tertiary amines, such as trimethylamine, triethylamine, tetramethylethylenediamine and cyclic tertiary amines. Examples of phosphines and phosphoramides include triphenylphosphine and hexamethylphosphoramide.

[0027]

In the present invention, the reaction temperature for the copolymerization for producing the block copolymer is generally in the range of from -10 to 150 °C, preferably from 30 to 120 °C. The reaction time for the copolymerization varies depending on other conditions, but is generally within 48 hours, preferably from 0.5 to 10 hours. It is preferred that the atmosphere of the copolymerization reaction system is an atmosphere of an inert gas, such as nitrogen gas. With respect to the copolymerization reaction pressure, there is no particular limitation so long as the pressure is suffi-

cient for the monomers and the solvent to maintain a liquid state. Further, care must be taken so as to prevent the intrusion of impurities (such as water, oxygen and carbon dioxide), which deactivate the catalyst and the living polymer, into the copolymerization reaction system.

[0028]

In the present invention, the modified block copolymer or hydrogenation product thereof as the component (1-1) comprises at least one polymer block A, at least one polymer block B, and at least one modifier group having at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, an amino group, a silanol group and an alkoxysilane group, wherein the modifier group is bonded to at least one member selected from the group consisting of the polymer block A and the polymer block B.

The modified block copolymer having bonded thereto at least one modifier group having at least one functional group can generally be produced by a method in which a living terminal of a block copolymer is reacted with a modifier compound having at least one functional group, wherein the functional group may be protected by a conventional method. As another method for producing the modified block copolymer, there can be mentioned a method in which a block copolymer is

reacted with an organic alkali metal compound (this reaction is called a "metalation reaction"), thereby obtaining a block copolymer having bonded thereto an alkali metal, followed by a reaction of the obtained block copolymer with a modifier compound. In this method, it is preferred that the block copolymer is hydrogenated before the metalation reaction and the subsequent reaction of the block copolymer with the modifier compound are performed. When the block copolymer is reacted with a modifier compound to obtain a modified block copolymer having a modifier group, it is possible that a hydroxyl group and an amino group which are contained in the modifier group are converted to organic alkali metal salts thereof, depending on the type of the modifier compound. In such case, the alkali metal salts can be reconverted to a hydroxyl group and an amino group by reacting the alkali metal salts with an active hydrogen-containing compound, such as water or an alcohol.

[0029]

In the present invention, a modified block copolymer (1-1) obtained by a reaction of a living terminal of the block copolymer with the modifier compound may contain an unmodified block copolymer fraction. It is recommended that the amount of such unmodified block copolymer fraction in the

modified block copolymer (1-1) is not more than 70 % by weight, preferably not more than 60 % by weight, more preferably not more than 50 % by weight.

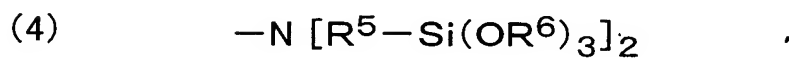
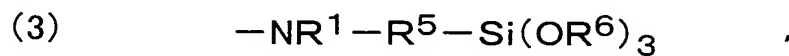
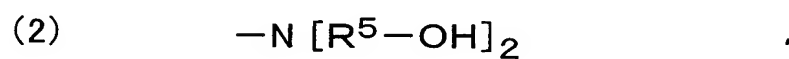
In the asphalt composition containing the component (1-1), the modifier group bonded to the block copolymer or hydrogenation product thereof has at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, an amino group, a silanol group and an alkoxysilane group. By virtue of any of the above-mentioned functional groups, the modified block copolymer has a high affinity for an asphalt, and interactions between the modified block copolymer and the asphalt are effectively caused to occur due to chemical bonds, such as a hydrogen bond between the modified block copolymer and components of the asphalt, thereby exerting the effects aimed at by the present invention. In the case of the asphalt composition containing the component (1-2), the same interactions as mentioned above are effectively caused, thereby exerting the effects aimed at by the present invention.

[0030]

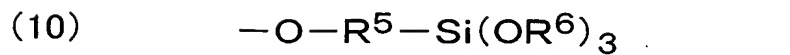
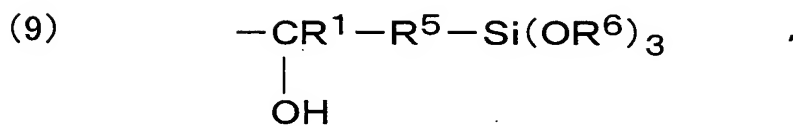
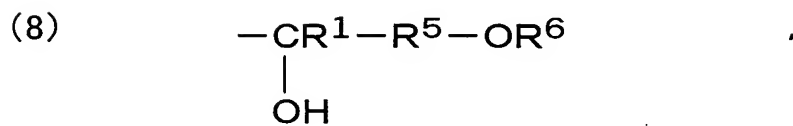
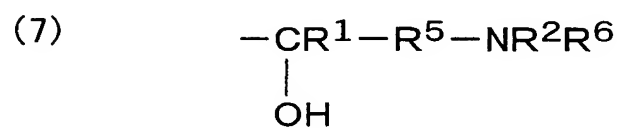
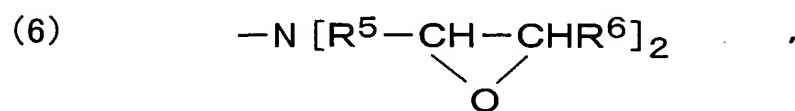
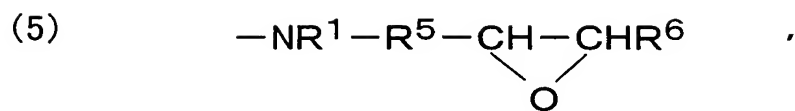
It is preferred that the modified block copolymer or hydrogenation product thereof as the component (1-1) has at least one modifier group having at least one functional group

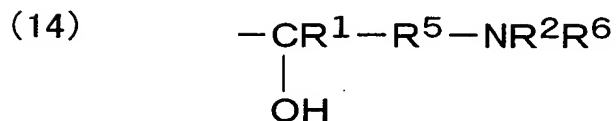
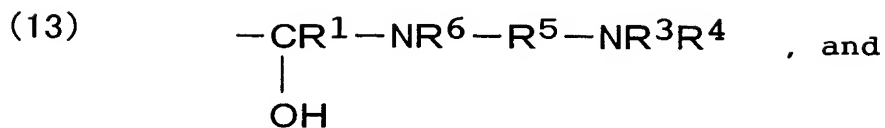
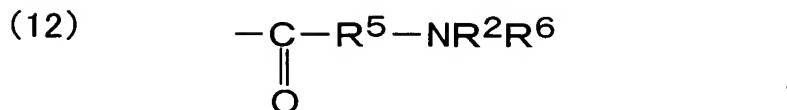
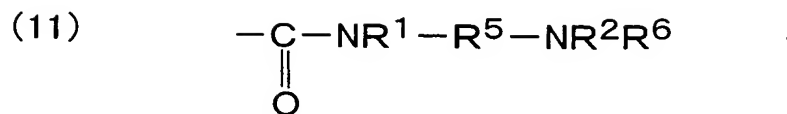
selected from the group consisting of the functional groups represented by the following formulae (1) to (14):

[0031]









[0032]

wherein, in the formulae (1) to (14):

each of  $\text{R}^1$  to  $\text{R}^4$  independently represents a hydrogen atom or a  $\text{C}_1$ - $\text{C}_{24}$  hydrocarbon group which optionally has at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, a silanol group and an

alkoxysilane group,

each  $R^5$  independently represents a  $C_1$ - $C_{48}$  hydrocarbon group which optionally has at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, a silanol group and an alkoxysilane group, and

each  $R^6$  independently represents a hydrogen atom or a  $C_1$ - $C_8$  alkyl group,

wherein the hydrocarbon group as each of  $R^1$  to  $R^5$  optionally has bonded thereto at least one atom selected from the group consisting of an oxygen atom, a nitrogen atom and a silicon atom, the at least one atom being present in a form which is different from those of a hydroxyl group, an epoxy group, a silanol group and an alkoxysilane group.

[0033]

In the present invention, examples of modifier compounds used for obtaining the block copolymer or hydrogenation product thereof (1) having at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, an amino group, a silanol group and an alkoxysilane group include the following modifier compounds:

[0034]

tetraglycidyl-m-xylene-diamine, tetraglycidyl-1,3-bisaminomethylcyclohexane, tetraglycidyl-p-phenylenediamine, tetraglycidyl-diaminodiphenylmethane, diglycidylaniline, diglycidyl-o-toluidine,  $\gamma$ -glycidoxyethyltrimethoxysilane,  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxybutyltrimethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane,

[0035]

$\gamma$ -glycidoxypropyltripropoxysilane,  $\gamma$ -glycidoxypropyltributoxysilane,  $\gamma$ -glycidoxypropyltriphenoxysilane,  $\gamma$ -glycidoxypropylmethyldimethoxysilane,  $\gamma$ -glycidoxypropylethyldimethoxysilane,  $\gamma$ -glycidoxypropylethyldiethoxysilane,  $\gamma$ -glycidoxypropylmethyldiethoxysilane,  $\gamma$ -glycidoxypropylmethyldipropoxysilane,  $\gamma$ -glycidoxypropylmethyldibutoxysilane,  $\gamma$ -glycidoxypropylmethyldiphenoxysilane,  $\gamma$ -glycidoxypropyldimethylmethoxysilane,  $\gamma$ -glycidoxypropyldiethylethoxysilane,  $\gamma$ -glycidoxypropyldimethylethoxysilane,

[0036]

$\gamma$ -glycidoxypropyldimethylphenoxysilane,  
 $\gamma$ -glycidoxypropyldiethylmethoxysilane,  
 $\gamma$ -glycidoxypropylmethyldiisopropeneoxysilane,  
bis( $\gamma$ -glycidoxypropyl)dimethoxysilane,  
bis( $\gamma$ -glycidoxypropyl)diethoxysilane,  
bis( $\gamma$ -glycidoxypropyl)dipropoxysilane,  
bis( $\gamma$ -glycidoxypropyl)dibutoxysilane,  
bis( $\gamma$ -glycidoxypropyl)diphenoxysilane,  
bis( $\gamma$ -glycidoxypropyl)methylmethoxysilane,  
bis( $\gamma$ -glycidoxypropyl)methylethoxysilane, bis( $\gamma$ -glycidoxy-  
propyl)methylpropoxysilane,  
bis( $\gamma$ -glycidoxypropyl)methylbutoxysilane,  
bis( $\gamma$ -glycidoxypropyl)methylphenoxysilane,

[0037]

tris( $\gamma$ -glycidoxypropyl)methoxysilane,  
 $\gamma$ -methacryloxypropyltrimethoxysilane,  
 $\gamma$ -methacryloxypropyltriethoxysilane,  
 $\gamma$ -methacryloxymethyltrimethoxysilane,  
 $\gamma$ -methacryloxyethyltriethoxysilane,  
bis( $\gamma$ -methacryloxypropyl)dimethoxysilane,  
tris( $\gamma$ -methacryloxypropyl)methoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-trimethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-triethoxysilane,

$\beta$ -(3,4-epoxycyclohexyl)ethyl-tripropoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-tributoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-triphenoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)propyl-trimethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-methyldimethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-ethyldimethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-ethyldiethoxysilane,

[0038]

$\beta$ -(3,4-epoxycyclohexyl)ethyl-methyldiethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-methyldipropoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-methyldibutoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-methyldiphenoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-dimethylmethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-diethylethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-dimethylethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-dimethylpropoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-dimethylbutoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-dimethylphenoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-diethylmethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyl-methyldiisopropeneoxysilane,  
 1,3-dimethyl-2-imidazolidinone, 1,3-diethyl-2-imidazolidinone,  
 N,N'-dimethylpropyleneurea and N-methylpyrrolidone.

[0039]

By reacting the block copolymer with the modifier compound, there can be obtained a modified block copolymer or hydrogenation product thereof (1-1) having at least one modifier group having at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, an amino group, a silanol group and an alkoxysilane group, wherein the modifier group is bonded to at least one member selected from the group consisting of the polymer block A and the polymer block B. With respect to the position in the modified block copolymer or hydrogenation product thereof at which the modifier group is bonded to the block copolymer, there is no particular limitation. However, from the viewpoint of obtaining an asphalt composition having excellent properties at high temperatures, it is preferred that the modifier group is bonded to the polymer block A.

[0040]

In the present invention, the hydrogenation product of the modified block copolymer can be obtained by hydrogenating the above-obtained modified block copolymer. With respect to the hydrogenation catalyst, there is no particular limitation, and any of the conventional hydrogenation catalysts can be used. Examples of hydrogenation catalysts include: (1) a carried, heterogeneous hydrogenation catalyst comprising a

carrier (such as carbon, silica, alumina or diatomaceous earth) having carried thereon a metal, such as Ni, Pt, Pd or Ru; (2) the so-called Ziegler type hydrogenation catalyst which uses a transition metal salt (such as an organic acid salt or acetylacetonate salt of a metal, such as Ni, Co, Fe or Cr) in combination with a reducing agent, such as an organoaluminum compound; and (3) a homogeneous hydrogenation catalyst, such as the so-called organometal complex, e.g., an organometal compound containing a metal, such as Ti, Ru, Rh or Zr. Specific examples of hydrogenation catalysts include those which are described in Examined Japanese Patent Application Publication Nos. Sho 42-8704, Sho 43-6636, Sho 63-4841, Hei 1-37970, Hei 1-53851 and Hei 2-9041. As preferred examples of hydrogenation catalysts, there can be mentioned a titanocene compound and a mixture of a titanocene compound and a reductive organometal compound.

[0041]

Examples of titanocene compounds include those which are described in Unexamined Japanese Patent Application Laid-Open Specification No. Hei 8-109219. As specific examples of titanocene compounds, there can be mentioned compounds (e.g., biscyclopentadienylyltitanium dichloride and monopentamethylcyclopentadienylyltitanium trichloride) which have at least one



ligand having a (substituted) cyclopentadienyl skeleton, an indenyl skeleton or a fluorenyl skeleton. Examples of reductive organometal compounds include organic alkali metal compounds, such as an organolithium compound; an organomagnesium compound; an organoaluminum compound; an organoboron compound; and an organozinc compound.

[0042]

The hydrogenation reaction is performed generally at 0 to 200 °C, preferably at 30 to 150 °C. It is recommended that the hydrogen pressure in the hydrogenation reaction is in the range of from 0.1 to 15 MPa, preferably from 0.2 to 10 MPa, more preferably from 0.3 to 5 MPa. The hydrogenation reaction time is generally in the range of from 3 minutes to 10 hours, preferably from 10 minutes to 5 hours. The hydrogenation reaction may be performed either in a batchwise manner or in a continuous manner. Further, the hydrogenation reaction may be performed in a manner wherein a batchwise operation and a continuous operation are used in combination.

[0043]

When the modified block copolymer is subjected to hydrogenation, there is no particular limitation with respect to the hydrogenation ratio as measured with respect to the unsaturated double bonds in the conjugated diene monomer units,

and the hydrogenation ratio can be adjusted to a desired level, depending on the desired properties of the asphalt composition. In some cases, the hydrogenation ratio is 70 % or more, preferably 80 % or more, more preferably 90 % or more. In other cases, the hydrogenation ratio is low. In such cases, the hydrogenation ratio is from 10 % to less than 70 %, preferably from 15 % to less than 65 %, more preferably from 20 % to less than 60 %. With respect to the hydrogenation ratio as measured with respect to the vinyl bonds in the conjugated diene monomer units, from the viewpoint of obtaining an asphalt composition having excellent heat stability, it is recommended that the hydrogenation ratio is 85 % or more, preferably 90 % or more, more preferably 95 % or more. Herein, the hydrogenation ratio with respect to the vinyl bonds is the percentage of the number of hydrogenated vinyl bonds, based on the number of the vinyl bonds in the conjugated diene monomer units of the block copolymer prior to hydrogenation.

[0044]

With respect to the hydrogenation ratio as measured with respect to the aromatic double bonds in the vinyl aromatic hydrocarbon monomer units of the block copolymer, there is no particular limitation. However, it is preferred that the hy-

drogenation ratio is 50 % or less, more advantageously 30 % or less, still more advantageously 20 % or less. With respect to the modified block copolymer or hydrogenation product thereof, the weight average molecular weight thereof is generally from 30,000 to 1,000,000, preferably from 50,000 to 800,000, more preferably from 70,000 to 600,000. When the weight average molecular weight of the modified block copolymer or hydrogenation product thereof is smaller than 30,000, the asphalt composition has neither a satisfactorily high softening point nor satisfactorily high mechanical strength. On the other hand, when the weight average molecular weight of the modified block copolymer or hydrogenation product thereof is larger than 1,000,000, the solubility of the modified block copolymer in the asphalt used in the asphalt composition becomes poor.

[0045]

In the present invention, the amount of vinyl bonds in the conjugated diene monomer units of the block copolymer can be measured by a method using an infrared spectrophotometer (e.g., the Hampton method) or by a method using a nuclear magnetic resonance (NMR) apparatus. Each of the above-mentioned hydrogenation ratios can also be measured by a method using an infrared spectrophotometer or an NMR appara-

tus. The weight average molecular weight of the modified block copolymer or hydrogenation product thereof can be measured by gel permeation chromatography (GPC) as follows. The block copolymer is subjected to GPC to obtain a chromatogram. The molecular weight of a peak in the chromatogram is obtained using a calibration curve obtained with respect to commercially available standard polystyrene samples. When the chromatogram has a plurality of peaks, the molecular weights of the peaks and the ratio between the peaks are taken into consideration, wherein the ratio between the peaks is calculated from the ratio between the areas of the peaks in the chromatogram.

[0046]

By the method described hereinabove, a modified block copolymer or hydrogenation product thereof is obtained in the form of a solution thereof in a solvent. From the obtained solution, the modified block copolymer or hydrogenation product thereof is separated. If desired, before the separation of the modified block copolymer or hydrogenation product thereof, a catalyst residue may be separated from the solution. Examples of methods for separating the modified block copolymer or hydrogenation product thereof from the solution include a method in which a polar solvent (which is a poor

solvent for the copolymer), such as acetone or an alcohol, is added to the solution containing the copolymer, thereby precipitating the copolymer, followed by recovery of the copolymer; a method in which the solution containing the copolymer is added to hot water while stirring, followed by removal of the solvent by steam stripping; and a method in which the solution containing the copolymer is directly heated to evaporate the solvent. The modified block copolymer or hydrogenation product thereof contains at least one stabilizer. Examples of stabilizers include phenol type stabilizers, phosphorus type stabilizers, sulfur type stabilizers and amine type stabilizers.

[0047]

With respect to the asphalt composition of the present invention, it is preferred that the modified block copolymer or hydrogenation product thereof as the component (1-1) is a block copolymer mixture of:

10 to 90 % by weight (more advantageously 20 to 80 % by weight) of a modified block copolymer or hydrogenation product thereof (1-A) comprising one polymer block composed mainly of vinyl aromatic hydrocarbon monomer units and one polymer block composed mainly of conjugated diene monomer units, and

90 to 10 % by weight (more advantageously 80 to 20 % by weight) of a modified block copolymer or hydrogenation product thereof (1-B) comprising at least two polymer blocks composed mainly of vinyl aromatic hydrocarbon monomer units, at least one polymer block composed mainly of conjugated diene monomer units, and the modifier group defined in the present invention,

[0048]

or a block copolymer mixture of:

10 to 90 % by weight (more advantageously 20 to 80 % by weight) of a modified block copolymer or hydrogenation product thereof (1-C) comprising one polymer block composed mainly of vinyl aromatic hydrocarbon monomer units, one polymer block composed mainly of conjugated diene monomer units, and the modifier group defined in the present invention, and

90 to 10 % by weight (more advantageously 80 to 20 % by weight) of a modified block copolymer or hydrogenation product thereof (1-D) comprising at least two polymer blocks composed mainly of vinyl aromatic hydrocarbon monomer units, at least one polymer block composed mainly of conjugated diene monomer units, and the modifier group defined in the present invention. The use of such block copolymer mixture is recommended from the viewpoint of obtaining an asphalt composition

exhibiting an excellent balance of high softening point and the anti-phase separation property.

[0049]

With respect to the weight average molecular weights of the components (1-A), (1-B), (1-C) and (1-D) as measured by GPC using a calibration curve obtained with respect to standard polystyrene samples, from the viewpoint of obtaining an asphalt composition exhibiting an excellent balance of high softening point and the anti-phase separation property, it is preferred that each of the weight average molecular weights of the components (1-A) and (1-C) is from 30,000 to 150,000, more advantageously from 40,000 to 140,000, still more advantageously from 50,000 to 130,000, and each of the weight average molecular weights of the components (1-B) and (1-D) is from 100,000 to 300,000, more advantageously from 120,000 to 280,000, still more advantageously from 140,000 to 260,000.

[0050]

Each of the block copolymer mixture comprising the components (1-A) and (1-B) and the block copolymer mixture comprising the components (1-C) and (1-D) can be obtained, for example, by a method in which the components are separately produced and the produced components are mixed together, wherein the production of each of the components is produced

by a method in which styrene monomers and then butadiene monomers are polymerized in an inert hydrocarbon solvent using an organolithium compound as a polymerization initiator (if desired, such polymerization is repeated), and the resultant copolymer is optionally reacted with a modified compound.

In this method, the weight average molecular weights of the components can be adjusted by appropriately choosing the amount of the organolithium compound used in the production of the components. The mixing of the components can be performed, for example, by the following method. By the above-described method, the components are individually obtained in the form of a solution thereof in a solvent. A deactivating agent (such as water, an alcohol or an acid) is added to the solutions to deactivate the active species in the solutions. The thus treated solutions are mixed together in a predetermined ratio. From the resultant mixture is removed the polymerization solvent by steam stripping or the like, followed by drying, thereby obtaining a block copolymer mixture. Alternatively, the above-mentioned block copolymer mixture can also be obtained by the following method. The polymerization solvents are respectively separated from the above-mentioned solutions in which the active species have been deactivated, to recover the copolymers, followed by drying to obtain dried



copolymers. The dried copolymers are mixed together using a roll or the like to obtain a block copolymer mixture.

[0051]

Further, each of the block copolymer mixture comprising the components (1-A) and (1-B) and the block copolymer mixture comprising the components (1-C) and (1-D) can be obtained can be produced by methods other than mentioned above. For example, the component (1-A) or (1-C) is obtained by the above-mentioned method. Then, one of the above-mentioned modifier compounds which are capable of undergoing a coupling reaction is added to the polymerization reaction system, wherein the amount ratio of the modifier compound to the organolithium compound is predetermined. By the addition of such modifier compound to the polymerization reaction system, a copolymer product is obtained (this copolymer product is referred to as "block copolymer (1-B)" or "block copolymer (1-C)"). Thus, a desired block copolymer mixture is obtained in a single polymerization reaction system.

[0052]

As asphalts as the component (2) used in the present invention, there can be mentioned a petroleum asphalt (i.e., asphalt by-produced by oil refining), natural asphalt, and mixtures thereof with petroleum. Each of the above-mentioned

asphalts contains bitumen as the main component thereof. Specific examples of asphalts include a straight asphalt, a semi-blown asphalt, a blown asphalt, tar, pitch, a cutback asphalt (i.e., a mixture of asphalt with oil), and an asphalt emulsion. These asphalts can be used individually or in combination.

[0053]

In the present invention, as a preferred asphalt, there can be mentioned a straight asphalt having a penetration ratio of from 30 to 300, preferably from 40 to 200, more preferably from 45 to 150. The amount of the modified block copolymer or hydrogenation product thereof as the component (1-1) of the asphalt composition of the present invention is from 0.5 to 50 parts by weight, preferably from 1 to 30 parts by weight, more preferably from 3 to 20 parts by weight, relative to 100 parts by weight of the asphalt.

As sulfur products used as the component (3), there can be mentioned a powdery sulfur, a precipitated sulfur, a colloidal sulfur, a surface-treated sulfur, an insoluble sulfur and an inert sulfur. As the component (3), there can also be used sulfur-containing compounds, such as sulfur chloride, sulfur dioxide, morpholine disulfide, an alkylphenol disulfide and a high molecular weight polysulfide. A crosslinking

accelerator can be used in an appropriate amount in combination with the sulfur (3). Examples of crosslinking accelerators include a sulfenamide type accelerator, a guanidine type accelerator, a thiuram type accelerator, an aldehyde-amine type accelerator, an aldehyde-ammonia type accelerator, a thiazole type accelerator, a thiourea type accelerator, a dithiocarbamate type accelerator and a xanthate type accelerator.

[0054]

Specific examples of such crosslinking accelerators include a diphenylguanidine, n-butyl aldehyde-anil condensate, a hexamethylenetetramine, 2-mercaptobenzothiazole, N-cyclohexyl-2-benzothiazyl sulfenamide, thiocarbanilide, tetramethylthiuram monosulfide, sodium dimethyl dithiocarbamate and zinc isopropyl xanthogenate. The amount of the sulfur as the component (3) is in the range of from 0.01 to 10 parts by weight, preferably from 0.05 to 5 parts by weight, more preferably from 0.1 to 2 parts by weight, relative to 100 parts by weight of the asphalt as the component (2). The amount of the crosslinking accelerator is in the range of from 0.01 to 10 parts by weight, preferably from 0.05 to 5 parts by weight, more preferably from 0.1 to 2 parts by weight, relative to 100 parts by weight of the asphalt as the

component (2).

[0055]

In the present invention, there is also provided an asphalt composition containing a second-order modified block copolymer as component (1-2) and the asphalt as the component (2). The second-order modified block copolymer (1-2) is obtained by reacting the component (1-1) with the crosslinking agent (4), wherein the component (1-1) is a modified block copolymer or hydrogenation product thereof which comprises a polymer block A, a polymer block B and at least one modifier group having at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, an amino group, a silanol group and an alkoxysilane group, and wherein the modifier group is bonded to at least one member selected from the group consisting of the polymer block A and the polymer block B. The amount of the component (4) is from 0.3 to 10 mol, preferably from 0.4 to 5 mol, more preferably from 0.5 to 4 mol, relative to one equivalent of the functional group of the component (1-1).

[0056]

As examples of methods for reacting the component (1-1) with the component (4), there can be mentioned a method using melt-kneading and a method in which the components are re-

acted with each other in a state in which they are dissolved or dispersed together in a solvent. The amount of the second-order modified block copolymer as the component (1-2) is from 0.5 to 50 parts by weight, preferably from 1 to 30 parts by weight, more preferably from 3 to 20 parts by weight, relative to 100 parts by weight of the asphalt as the component (2). When both the components (1-2) and (2) are used in the asphalt composition, the amount of the component (4) is from 0.01 to 20 parts by weight, preferably from 0.02 to 10 parts by weight, more preferably from 0.05 to 7 parts by weight, relative to 100 parts by weight of the component (2).

[0057]

In the present invention, the crosslinking agent as the component (4) is a crosslinking agent having a functional group which is reactive to the functional group of the modified block copolymer or hydrogenation product thereof as the component (1-1). As a preferred example of the crosslinking agent (4), there can be mentioned a crosslinking agent having at least one functional group selected from the group consisting of a carboxyl group, an acid anhydride group, an isocyanate group, an epoxy group, a silanol group and an alkoxysilane group. It is especially preferred that the crosslinking agent (4) has at least two functional groups se-

lected from the group consisting of the above-mentioned functional groups.

[0058]

Specific examples of crosslinking agents (4) are enumerated below. Examples of crosslinking agents having at least two carboxyl groups include oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid and terephthalic acid. These carboxylic acids can be used also in the form of an acid anhydride. Examples of such acid anhydrides include maleic anhydride, succinic anhydride and phthalic anhydride.

[0059]

Examples of crosslinking agents (4) having at least two acid anhydride groups include 1,2,4,5-benzenetetracarboxylic acid dianhydride, 5-(2,5-dioxytetrahydroxy-furyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride, and a trimellitic anhydride mixture. Examples of crosslinking agents (4) having at least two isocyanate groups include toluylene diisocyanate, diphenylmethane diisocyanate and multifunctional aromatic isocyanates. Examples of crosslinking agents (4) having at least two silanol groups include hydrolysis products of silane compounds which are exemplified

as modifier compounds used for producing the modified block copolymer as the component (1-1). Examples of crosslinking agents (4) having at least two alkoxy silane groups include bis-(3-triethoxysilylpropyl)-tetrasulfane, ethoxysiloxane oligomers, and silane compounds which are exemplified as modifier compounds used for producing the modified block copolymer as the component (1-1).

[0060]

Examples of crosslinking agents (4) having at least two epoxy groups include ethylene glycol diglycidyl, propylene glycol diglycidyl, terephthalic acid diglycidyl ester acrylate, and epoxy compounds which are exemplified as modifier compounds used for producing the modified block copolymer as the component (1-1). Especially preferred examples of crosslinking agents (4) include maleic anhydride, 1,2,4,5-benzenetetracarboxylic acid dianhydride, toluylene diisocyanate and tetraglycidyl-1,3-bisaminomethylcyclohexane.

[0061]

The asphalt composition of the present invention may contain a silane coupling agent. Specific examples of silane coupling agents include bis[3-(triethoxysilyl)propyl]tetrasulfide, bis[3-(triethoxysilyl)propyl]disulfide, bis[2-(triethoxysilyl)ethyl]tetrasulfide, 3-mercaptopropyl-

trimethoxysilane, 3-mercaptopropyl-methyldimethoxysilane, 3-triethoxysilylpropyl-N,N-dimethylthiocarbamoyltetrasulfide and 3-triethoxysilylpropylbenzothiazoletetrasulfide.

[0062]

Further specific examples of silane coupling agents include vinyltrimethoxysilane, vinyltriethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, 3-glycidoxypropyltriethoxysilane, p-styryltrimethoxysilane, 3-methacryloxypropyl-methyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropylmethyldiethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrimethoxysilane, N-2(aminoethyl)3-aminopropylmethyldimethoxysilane, N-2(aminoethyl)3-aminopropyltrimethoxysilane and N-2(aminoethyl)3-aminopropyltriethoxysilane.

[0063]

Further specific examples of silane coupling agents include 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-triethoxysilyl-N-(1,3-dimethylbutylidene)propylamine, N-phenyl-3-aminopropyltrimethoxysilane and 3-isocyanatepropyltriethoxysilane.

As a preferred example of the silane coupling agent,



there can be mentioned a compound having a polysulfide linkage containing a silanol group or an alkoxysilane in combination with two or more of a mercapto group and/or a sulfur atom. Specific examples of such preferred silane coupling agents include bis[3-(triethoxysilyl)propyl]tetrasulfide, bis[3-(triethoxysilyl)propyl]disulfide, bis[2-(triethoxysilyl)ethyl]tetrasulfide, 3-mercaptopropyl-trimethoxysilane, 3-mercaptopropyl-methyldimethoxysilane, 3-triethoxysilylpropyl-N,N-dimethylthiocarbamoyltetrasulfide and 3-triethoxysilylpropylbenzothiazoletetrasulfide. It is recommended that the amount of the silane coupling agent is from 0.01 to 20 parts by weight, preferably from 0.05 to 10 parts by weight, more preferably from 0.1 to 5 parts by weight, relative to 100 parts by weight of the asphalt as the component (2).

[0064]

If desired, the asphalt composition of the present invention may contain any of the conventional additives. With respect to the type of the additive, there is no particular limitation so long as it is an additive which is generally used in combination with a thermoplastic resin or a rubbery copolymer. Examples of additives include inorganic fillers, such as calcium carbonate, magnesium carbonate, magnesium hy-

dioxide, calcium sulfate, barium sulfate, silica, clay, talc, mica, wollastonite, montmorillonite, zeolite, alumina, titanium oxide, magnesium oxide, zinc oxide, a slag wool and a glass fiber.

[0065]

Further examples of additives include those which are described in "Gomu Purasuchikku Haigou Yakuhin (Additives for Rubber and Plastic)" (published by Rubber Digest Co., Ltd.). Specific examples of such additives include pigments, such as carbon black and an iron oxide; lubricants, such as stearic acid, behenic acid, zinc stearate, calcium stearate, magnesium stearate and ethylenebisstearoamide; mold release agents; softening agents and plasticizers, such as a paraffinic process oil, a naphthenic process oil, an aromatic process oil, a paraffin, an organic polysiloxane and a mineral oil; antioxidants, such as a hindered phenol type antioxidant and a phosphorus type thermal stabilizer; hindered amine type light stabilizers; benzotriazole type ultraviolet absorbers; flame retardants; antistatic agents; reinforcing agents, such as an organic fiber, a glass fiber, a carbon fiber and a metal whisker; coloring agents; additives other than mentioned above; and mixtures thereof.

[0066]

[Mode for Carrying Out the Invention]

Hereinbelow, the present invention will be described in more detail with reference to the following Examples, which should not be construed as limiting the scope of the present invention.

In the Examples, the properties of block copolymers, hydrogenation products thereof and asphalt compositions were determined by the following methods.

A. Properties of modified block copolymers and the like

1) Styrene content

The absorption intensity was measured at 262 nm using an ultraviolet spectrophotometer (trade name: UV200; manufactured and sold by Hitachi, Ltd.), and the styrene content was calculated therefrom.

2) Vinyl bond content and hydrogenation ratio

The vinyl bond content and hydrogenation ratio were measured by means of a nuclear magnetic resonance apparatus (trade name: DPX-400; manufactured and sold by BRUKER).

[0067]

3) Molecular weight

The weight average molecular weight was measured by GPC using a GPC apparatus (manufactured and sold by Waters Corporation) and a column packed with a polystyrene gel, under

conditions wherein tetrahydrofuran was used as a solvent and the measuring temperature was 35 °C. In the measurement of the weight average molecular weight, the molecular weight of a peak in a chromatogram obtained by GPC was calculated, using a calibration curve obtained with respect to commercially available standard polystyrene samples. When the chromatogram has a plurality of peaks, the molecular weights of the peaks and the ratio between the peaks are taken into consideration, wherein the ratio of the peaks is calculated from the ratio between the areas of the peaks in the chromatogram.

[0068]

4) Amount of the unmodified block copolymer fraction

A modified copolymer adsorbs on a silica gel column. Based on such a unique property of the modified copolymer, the modification ratio of the modified copolymer was determined as follows. A sample solution containing a modified copolymer sample and a low molecular weight internal standard polystyrene was prepared and the prepared sample solution was subjected to GPC using the standard type polystyrene gel column and the GPC apparatus used in item 3) above, to thereby obtain a chromatogram. On the other hand, the same sample solution was subjected to GPC in substantially the same manner as mentioned above, except that a silica gel column

(trade name: Zorbax; manufactured and sold by DuPont) was used. From the chromatogram obtained using the polystyrene gel column and the chromatogram obtained using the silica gel column, the amount of modified copolymers adsorbed on the silica gel column was determined, from which the amount of the unmodified block copolymer fraction was obtained.

[0069]

B. Production of modified block copolymers and the like

The hydrogenation catalyst used in hydrogenation reactions was prepared by the following method.

A reaction vessel was purged with nitrogen. To the reaction vessel were added two liters of dried, purified cyclohexane. Then, 40 mmol of bis( $\eta^5$ -cyclopentadienyl)titanium-di(p-tolyl) and 150 g of a 1,2-polybutadiene having a molecular weight of about 1,000 and a 1,2-vinyl bond content of about 85 % were added to and dissolved in the cyclohexane, thereby obtaining a solution. A cyclohexane solution of 60 mmol of n-butyllithium was added to the solution in the reaction vessel, and a reaction was performed at room temperature for 5 minutes, and then 40 mmol of n-butanol was immediately added to the reaction vessel while stirring, thereby obtaining a hydrogenation catalyst. The obtained hydrogenation catalyst was preserved at room temperature.

[0070]

a. Polymer 1

An autoclave equipped with a stirrer and a jacket was washed, dried and purged with nitrogen. To the autoclave was added a cyclohexane solution of 15 parts by weight of purified styrene (styrene concentration: 20 % by weight). n-Butyllithium and tetramethylethylenediamine were added to the autoclave. Then, a polymerization reaction was performed at 70 °C for 1 hour. Subsequently, a cyclohexane solution of 70 parts by weight of purified butadiene (butadiene concentration: 20 % by weight) was added to the autoclave, and a polymerization reaction was performed at 70 °C for 1 hour. Thereafter, a cyclohexane solution of 15 parts by weight of purified styrene (styrene concentration: 20 % by weight) was added to the autoclave, and a polymerization reaction was performed at 70 °C for 1 hour, thereby obtaining a living polymer.

[0071]

The obtained living polymer was reacted with 1,3-dimethyl-2-imidazolidinone as a modifier compound (hereinafter, this modifier compound is referred to as "modifier compound M1"), wherein the modifier compound was used in an amount equimolar to the n-butyllithium which was used above.

To the resultant reaction mixture were added methanol and, then, octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate as a stabilizer wherein the amount of the stabilizer was 0.3 part by weight, relative to 100 parts by weight of the above-obtained living polymer, thereby obtaining a modified block copolymer (polymer 1).

The obtained modified block copolymer (polymer 1) had a styrene content of 30 % by weight, a styrene block ratio of 95 % by weight, a vinyl bond content of 15 %, and a weight average molecular weight of 110,000.

[0071]

b. Polymer 2

A modified block copolymer (polymer 2) was produced in substantially the same manner as in the production of polymer 1, except that a cyclohexane solution of 12.5 parts by weight of styrene (styrene concentration: 20 % by weight) was added to the autoclave and a polymerization reaction was performed; a cyclohexane solution of 75 parts by weight of butadiene (butadiene concentration: 20 % by weight) was added to the autoclave and a polymerization reaction was performed; and a cyclohexane solution of 12.5 parts by weight of styrene (styrene concentration: 20 % by weight) was added to the autoclave and a polymerization reaction was performed. The ob-

tained polymer 2 had a styrene content of 25 % by weight, a styrene block ratio of 98 % by weight, a vinyl bond content of 13 %, and a weight average molecular weight of 130,000. To a cyclohexane solution of the obtained modified block copolymer was added maleic anhydride (hereinafter referred to as "crosslinking agent D1") in an amount equimolar to the functional group of the modified block copolymer, and a reaction was performed, thereby obtaining a second-order modified block copolymer (polymer 2). To polymer 2 was added octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate as a stabilizer wherein the amount of the stabilizer was 0.3 part by weight, relative to 100 parts by weight of polymer 2.

[0073]

#### C. Production of asphalt compositions

400 g of straight asphalt 60-80 (manufactured and sold by NIPPON OIL COMPANY, LIMITED) was added to a metal can having a volume of 750 ml. The metal can containing the straight asphalt was put into an oil bath having a temperature of 180 °C so that the straight asphalt was satisfactorily heated, thereby melting the asphalt. Then, to the resultant molten asphalt were added a predetermined amount of a block copolymer and the like bit by bit while stirring. After completion of the addition of the block copolymer and the



like, the resultant mixture was stirred at a revolution rate of 5,000 rpm for 90 minutes, thereby obtaining an asphalt composition.

[0074]

D. Properties of asphalt compositions

1) Softening point (ring-and-ball method)

The softening point of the asphalt composition was measured in accordance with JIS K 2207. Specifically, the ring of an apparatus as defined in JIS K 2207 is filled with a sample of the asphalt composition. The apparatus is immersed in glycerol, and the ring is maintained level in the glycerol. Then, a ball having a weight of 3.5 g is placed at the center of the ring filled with the sample. The temperature of the glycerol is elevated at a rate of 5 °C/min. The central portion of the softening sample is gradually sagged under the weight of the ball, and the temperature (softening point) at which the sagged central portion of the sample reaches a bottom plate placed below the ring is measured.

2) Melt viscosity

The melt viscosity was measured by means of a Brookfield viscometer at 180 °C.

3) Penetration ratio

The penetration ratio of the asphalt composition was

measured in accordance with JIS K 2207. Specifically, a sample of the asphalt composition is placed in a thermostatic water bath, and the temperature of the sample is maintained at 25 °C. Then, a prescribed needle is caused to penetrate into the sample for 5 seconds. The distance over which the needle has penetrated into the sample is measured, and is defined as the penetration ratio.

#### 4) Elongation

The elongation of the asphalt composition was measured in accordance with JIS K 2207. Specifically, a sample of the asphalt composition is poured into a mold to shape the sample into a prescribed form. Then, the shaped sample is placed in a thermostatic water bath, and the temperature of the sample is maintained at 4 °C. Then, the sample is pulled at a rate of 5 cm/min until it is broken, and the elongation of the sample at the time of breakage is measured.

[0075]

#### 5) Adhesion strength

The asphalt composition is dissolved in toluene, and the resultant solution is coated onto a canvas using a coater. The coated canvas is dried, first at room temperature for 1 hour, and then at 70 °C in an oven for 7 minutes, thereby completely evaporating the toluene from the coated canvas.

Subsequently, the coated canvas is placed in an oven together with a granite (as an adherend) having a smooth surface, and the coated canvas and the granite are heated at 70 °C for 1 hour. Then, the coated canvas and the granite are taken out from the oven and rapidly pressed onto each other twice using a roller under a load of 1 kg, thereby adhering the coated canvas onto the granite. The resultant structure in which the coated canvas is adhered onto the granite, is placed in a thermostatic chamber at a temperature of 23 °C, and a peeling test (peeling angle: 180°) in which the canvas is peeled off from the granite is performed to measure the adhesion strength of the asphalt composition.

[0076]

6) Flexural properties at low temperatures

The asphalt composition is poured into a mold having a size of 20 mm × 20 mm × 120 mm, and the excess asphalt composition is cut off. The mold containing the asphalt composition is placed in a cryostat, and the asphalt composition in the mold is maintained at -20 °C for 4 hours or more. Then, the resultant molded product of the asphalt composition is rapidly taken out from the mold, and is measured with respect to the flexural stress by a method in which the molded product is supported at two points thereof which are at a dis-

tance (span) of 80 mm from each other, and a load is applied, at a loading rate of 100 mm/min, to a portion of the molded product which is at a middle of the 80 mm span.

7) High temperature storage stability (separation characteristics)

An aluminum can having an inner diameter of 50 mm and a height of 130 mm is filled up with the asphalt composition immediately after the production thereof. The aluminum can containing the asphalt composition is placed in an oven and heated at 180 °C for 24 hours. The aluminum can is taken out from the oven and allowed to stand so that the asphalt composition in the aluminum can cools to room temperature. As samples, upper and lower portions of the resultant solidified asphalt composition, which are a 4 cm-thick lower layer at a lower end portion and a 4 cm-thick upper layer at an upper end portion, are taken by cutting. The softening points of both the samples are measured. The difference in softening point between the samples is used as a yardstick for the high temperature storage stability of the asphalt composition.

[0077]

[Examples 1 to 3 and Comparative Examples 1 to 4]

Asphalt compositions were produced in accordance with the formulations indicated in Table 1 (polymer 1 was used as

a block copolymer). Specifically, the production of each asphalt composition was performed as follows.

400 g of straight asphalt 60-80 (manufactured and sold by NIPPON OIL COMPANY, LIMITED) was added to a metal can having a volume of 750 ml. The metal can containing the straight asphalt was put into an oil bath having a temperature of 180 °C so that the straight asphalt was satisfactorily heated, thereby melting the asphalt. Then, to the resultant molten asphalt were added a predetermined amount of polymer 1 and a predetermined amount of sulfur (trade name: GOLDEN FLOWER SULFUR POWDER; manufactured and sold by Tsurumi Chemical Co.) bit by bit while stirring. After completion of the addition of polymer 1 and sulfur, the resultant mixture was stirred at a revolution rate of 5,000 rpm for 90 minutes, thereby obtaining an asphalt composition. The properties of the obtained asphalt composition are shown in Table 1.

[0078]

[Example 4]

An asphalt compositions was produced in accordance with the formulations indicated in Table 1 (polymer 2 was used as a block copolymer) in substantially the same manner as in Example 1. The properties of the obtained asphalt composition are shown in Table 1.

[0079]

[Table 1]

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Amount of block copolymer (parts by weight)		8	3	20	8	0.3	60	8	8
Amount of asphalt (parts by weight)		100	100	100	100	100	100	100	100
Amount of sulfur (parts by weight)		0.1	4	0.05	0.1	5	0.2	0	12
Softening point (°C)		93	87	99	91	54	Not measurable due to high viscosity	84	Not measurable due to high viscosity
Melt viscosity (cP)		570	420	595	470	250		410	
Penetration ratio (1/10 mm)		40	42	57	37	58		35	
Elongation (cm)		82	80	88	81	12		92	
Adhesion strength (gf/10 mm)		4,750	4,010	5,200	4,130	150	Not measurable due to high viscosity	2,920	Not measurable due to high viscosity
Flexural stress (N/mm <sup>2</sup> )		10.4	9.2	12.8	11.5	3.6		8.2	
High temperature storage stability	Difference in softening point (°C)	18	17	20	17	10	Not measurable due to high viscosity	22	Not measurable due to high viscosity

[0080]

[Effect of the Invention]

The asphalt composition of the present invention has a good balance of asphalt properties and has excellent storage stability at high temperatures.



[Name of Document]        Abstract

[Abstract]

[Task] A task of the present invention is to provide an asphalt composition having a good balance of softening point, ductility, flexural properties and aggregate-gripping properties and having excellent storage stability at high temperatures.

[Means to Solve the Problems] An asphalt composition comprising: 0.5 to 50 parts by weight of a modified block copolymer or hydrogenation product thereof, the modified block copolymer comprising at least one polymer block A composed mainly of vinyl aromatic hydrocarbon monomer units, at least one polymer block B composed mainly of conjugated diene monomer units, and at least one modifier group having at least one functional group selected from the group consisting of a hydroxyl group, an epoxy group, an amino group, a silanol group and an alkoxysilane group, wherein the modifier group is bonded to at least one member selected from the group consisting of the polymer block A and the polymer block B; 100 parts by weight of an asphalt; and 0.01 to 10 parts by weight of sulfur.

[Selected Figure]        None

Historical Information on Applicant

Identification Number	[000000033]
1. Date of Change	January 4, 2001
[Reason for Change]	Change of Name
Address:	2-6, Dojimahama 1-chome, Kita-ku Osaka-shi, Osaka
Name:	Asahi Kasei Kabushiki Kaisha